Methanotrophy potential versus methane supply by pore water diffusion in peatlands

E. R. C. Hornibrook, H. L. Bowes, A. Culbert, A. V. Gallego-Sala

Biogeosciences Discuss., 5, 2607–2643, 2008
www.biogeosciences-discuss.net/5/2607/2008/

Biogeosciences Discussions

Biogeosciences Discussions is the access reviewed discussion forum of *Biogeosciences*

Methanotrophy potential versus methane supply by pore water diffusion in peatlands

E. R. C. Hornibrook, H. L. Bowes, A. Culbert, and A. V. Gallego-Sala

Bristol Biogeochemistry Research Centre, Department of Earth Sciences, University of Bristol, Wills Memorial Building, Queens Road, Bristol, BS8 1RJ, UK

Received: 4 March 2008 – Accepted: 29 March 2008 – Published: 18 June 2008

Correspondence to: E. R. C. Hornibrook (ed.hornibrook@bristol.ac.uk)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Low affinity methanotrophic bacteria consume a significant quantity of methane in wetland soils in the vicinity of plant roots and at the oxic-anoxic interface. Estimates of the efficiency of methanotrophy in peat soils vary widely in part because of differences in approaches employed to quantify methane cycling. High resolution profiles of dissolved methane abundance measured during the summer of 2003 were used to quantify rates of upward methane flux in four peatlands situated in Wales, UK. Aerobic incubations of peat from a minerotrophic and an ombrogenous mire were used to determine depth distributions of kinetic parameters associated with methane oxidation. The capacity for methanotrophy in a 3 cm thick zone immediately beneath the depth of nil methane abundance in pore water was significantly greater than the rate of upward diffusion of methane in all four peatlands. Rates of methane diffusion in pore water at the minerotrophic peatlands were small (<10%) compared to surface emissions during June to August. The proportions were notably greater in the ombrogenous bogs because of their typically low methane emission rates. Methanotrophy appears to consume entirely methane transported by pore water diffusion in the four peatlands with the exception of 4 of the 33 gas profiles sampled. Flux rates to the atmosphere regardless are high because of gas transport through vascular flora, in particular, at the minerotrophic sites. Cumulative rainfall amount 3-days prior to sampling correlated well with the distance between the water table level and the depth of 0 μmol l^{-1} methane, indicating that precipitation events can impact methane distributions in pore water. Further work is needed to characterise the kinetics of methane oxidation spatially and temporally in different wetland types in order to determine generalized relationships for methanotrophy in peatlands that can be incorporated into process-based models of methane cycling in peat soils.

BGD

5, 2607–2643, 2008

1 Introduction

Alpha and gamma Proteobacteria belonging, respectively, to the Methylocystaceae and Methylococcaceae families are ubiquitous at oxic-anoxic interfaces in the Earth system where oxygen (O_2) is present and methane (CH_4) is transported in large quantities under the influence of concentration gradients or ebullition. These microorganisms, also known as Type I (gamma) and Type II (alpha) methanotrophs, serve as an efficient filter, removing CH_4 that otherwise would enter the troposphere. Collectively low affinity methanotrophs in such environments annually consume a quantity of CH_4 well in excess of the ~600 Tg that does enter the Earth's atmosphere from biological and geological sources (Mikaloff Fletcher et al., 2004).

The anoxic soils of natural wetlands are one of the main perennial sources of CH_4 flux that help to maintain a low but significant quantity of this chemically and radiatively active organic gas in the Earth's highly oxidizing atmosphere. More than three decades of study of methanotrophs in wetlands and peatlands have yielded significant insights into their phylogeny, distribution, kinetics, and preferred growth conditions (e.g., Segers, 1998; Gutknecht, 2006; Chen et al., 2008). Methanotroph populations in the rhizosphere and with depth in peat soils have been mapped using molecular biology techniques, including PCR amplification of DNA extracts and hybridisation with specific phylogenetic 16S rRNA and functional gene primers (e.g., Krumholz et al., 1995; McDonald et al., 1996, 1999; Ritchie et al., 1997; Calhoun and King, 1998; Edwards et al., 1998; Dedysh, 2002; Dedysh et al., 2001, 2003; Wartiainen et al., 2003; Miller et al., 2004), quantification of membrane phospholipid fatty acids (PLFAs) (Krumholz et al., 1995; Sundh et al., 1995, 1997), and more recently stable isotope probing techniques involving ^{13}C-labelling of PLFAs and nucleic acids (Morris et al., 2002; McDonald et al., 2005; Kreuzer-Martin, 2007; Chen et al., 2008). Both Type I and II methanotrophs occur in wetland soils, occupying oxic zones immediately adjacent to plant roots (King, 1994, 1996; Schipper and Reddy, 1996; Calhoun and King, 1998; van der Nat and Middelburg, 1998; Popp et al., 2000) and shallow zones within peat soils to which at-

BGD
5, 2607–2643, 2008

mospheric O_2 is able to diffuse under edaphic conditions and vegetation groundcover specific to particular types of wetlands (Krumholz et al., 1995; McDonald et al., 1996; Watson et al., 1997; Edwards et al., 1998; Beckman and Lloyd, 2001; Megonigal and Schlesinger, 2002).

The tolerance of methanotrophs to anoxia appears to vary (Roslev and King, 1996). Greatly diminished levels of methanotrophic activity have been reported in post-anoxia incubations of rhizome material (King, 1994) while sediment and peat from other wetlands upon return to O_2-rich conditions have shown CH_4 oxidation capacities ranging from moderately attenuated (e.g., King, 1990) to rapid and vigorous (Whalen and Reeburgh, 2000). Methane supply is most commonly cited as the factor limiting methanotrophy in peat soils (Boon and Lee, 1997; Megonigal and Schlesinger, 2002; Berestovskaya et al., 2005; Basiliko et al., 2007) although O_2 availability also may restrict rates of CH_4 uptake (King, 1990, 1994, 1996; Mikkelä et al., 1995; Beckman and Lloyd, 2001). Differences in the limiting factors between peatlands likely results from a combination of soil properties affecting gas exchange and heat transfer, the abundance and types of flora present, and water table depth, all of which impact the potential for CH_4 oxidation and production (Kettunen et al., 1996; Kettunen, 2003). Water table level is a particularly critical parameter because it controls the thickness of the unsaturated zone, which enhances the capacity for methanotrophy, but also can eliminate a key zone for CH_4 production at shallow depths in the vicinity of the rhizosphere where methanogens benefit from higher temperatures and an abundant supply of labile substrates from root exudation (Roulet et al., 1993; Sundh et al., 1994; Kettunen et al., 1999; Ström et al., 2005). Despite the presence of methanotrophy in this zone, CH_4 flux from wetlands is significantly enhanced by gas exchange with the atmosphere through the aerenchyma of vascular flora (Shannon et al., 1996; Joabsson et al., 1999; Joabsson and Christensen, 2001; Oquist and Svensson, 2002; Ström and Christensen, 2007). In the absence of high temporal resolution measurements of CH_4 flux capable of detecting sporadic ebullition events (Baird et al., 2004; Tokida et al., 2007a, b), estimates of CH_4 emission from wetlands will be dominated by passive or

active transport of CH_4 through vascular aquatic plants when suitable flora are present.

Attempts to quantify the efficiency of methanotrophy in peat soils have yielded a wide range of estimates of CH_4 consumption, in part, because of different methods employed and the limitations associated with specific approaches as discussed by Pearce and Clymo (2001). Le Mer and Roger (2001) concluded from a survey of literature that ~60 to 90% of CH_4 produced in wetland soils is oxidized by methanotrophs in the rhizosphere or shallow subsurface horizons; however, other estimates suggest a range of proportions, including 20–40% in general for natural wetlands (Whalen, 2005), 15 to 76% of potential diffusive CH_4 flux seasonally and ~43% annually of CH_4 entering the oxic zone of a freshwater marsh (Roslev and King, 1996), ~22% for conversion of CH_4 to CO_2 during transport through 10 cm of acrotelm *Sphagnum*-rich peat (Pearce and Clymo, 2001), complete consumption within 20 cm of the water table in an undrained peatland (Roulet et al., 1993), 65±24% of CH_4 entering the rhizosphere of *Sagittaria lancifolia* estimated by CH_3F inhibition and 79±20% by mass balance (Schipper and Reddy, 1996), 34.7±20.3% and 16.1±7.9% in the rhizosphere, respectively, of bulrush and reed wetlands (van der Nat and Middelburg, 1998), 55% of upward diffusing CH_4 in an Alaskan boreal peatland (Whalen and Reeburgh, 2000), 52±10% and 81±9% in two tidal freshwater wetland forests (Megonigal and Schlesinger, 2002), 0 to 34% rhizosphere oxidation of CH_4 in a *Carex* fen determined using ^{13}C mass balance (Popp et al., 1999), and 58 to 92% or <20% in the same peatland depending upon whether CH_4 consumption was quantified by subtracting in situ methane emission rates from CH_4 production rates measured in the laboratory or in situ use of the CH_3F inhibitor technique (Popp et al., 2000). Much of the variability in estimates of CH_4 oxidation efficiency appears to stem from differences in methodology. As noted by Popp et al. (2000), CH_4 production rates determined in vitro likely lead to an overestimation of CH_4 supply in peat soils, contributing to the calculation of anomalously high proportions of CH_4 removal by methanotroph activity.

We measured detailed (cm scale resolution) in situ profiles of dissolved CH_4 concentration at four different peatlands situated in Wales, UK during the summer of 2003 to

BGD

5, 2607–2643, 2008

calculate the supply of CH_4 into the methanotrophic zone at the sites. The gas concentration profiles enabled determination of complete attenuation of CH_4 flux by pore water diffusion when the abundance of dissolved CH_4 was $\sim 0\,\mu mol\,l^{-1}$ (i.e., below detection limits) within the saturated zone. We compared estimated rates of CH_4 transport by pore water diffusion to total quantites of CH_4 emitted to the atmosphere. We also used aerobic incubations of peat amended with CH_4 to assess differences in CH_4 uptake kinetics with depth and between two of the peatlands (a raised bog and an intermediate fen). In situ CH_4 concentration data and the determined μ_m (maximum rates of CH_4 oxidation) and K_s (half saturation concentrations) values were then employed to estimate the capacity for CH_4 consumption in relation to the supply of CH_4 by pore water diffusion. Finally, we also investigated relationships between cumulative rainfall in the period preceding pore water sampling and the distribution of CH_4 with depth in the peatland soils to determine whether the timing of sampling impacted our results.

2 Site characterisation

2.1 Peatland descriptions

The locations of the four peatlands investigated in Wales, UK are shown in Fig. 1 and further details for the sites are provided in Table 1. Crymlyn Bog and Gors Lywd both receive water input from surrounding uplands via overland and subsurface flow and thus have slightly more alkaline pore water than Blaen Fign and Cors Caron, which are ombrogeneous bogs. *Sphagnum* spp. were common at all sites; however, predictably the abundance and diversity of vascular flora were highest at the minerotrophic peatlands Crymlyn Bog and Gors Lywd. At each peatland, two adjacent stations (~1 m apart) were chosen for installation of pore water equilibrators and ground collars to support flux chambers. At Crymlyn Bog and Blaen Fign the ground collars enclosed significantly different proportions of bryophytes and vascular flora with *Sphagnum* moss dominating at station 1 and sedge species at station 2.

BGD
5, 2607–2643, 2008

2.2 Weather data

Daily precipitation data for the period January to December 2003 collected at UK Meteorological Office Stations at Swyddffynnon, Cwmystwyth, Llangurig and Swansea Victoria Park (Fig. 1) were obtained from the British Atmospheric Data Centre (BADC) archive.

3 Analytical methods

3.1 Sample collection

Pore water equilibrators and ground collars for flux chambers were installed at the sites several months prior to the onset of sampling which began in the spring of 2003. Measurements of in situ concentrations of pore water CH_4 and rates of CH_4 flux to the atmosphere were performed between April and September 2003 at the four peatlands. One peatland was sampled each week yielding on average one monthly data set for each site during the growing season. Peat cores were collected in September 2005 for follow-up experiments investigating differences in methane oxidation kinetics with depth at Cors Caron and Crymlyn Bog.

3.2 Methane flux

Collection methods and CH_4 flux data for all sites were reported previously in Bowes and Hornibrook (2006) and Hornibrook and Bowes (2007). Briefly, flux chambers and ground collars were constructed of polyvinyl chloride (PVC) and had a combined volume of either 11 or 15 litres. The chambers were sealed onto the collars using large neoprene rubber o-rings coated with silicon grease and then covered with opaque lids also fitted with greased o-rings. Air samples were collected via a 4-m length of 3-mm OD Tygon® tube installed in the lid of each chamber. A second identical tube fitted in

BGD
5, 2607–2643, 2008

the lid was kept open during sampling to prevent subambient pressures from forming while air samples were collected. Each chamber contained a small battery operated fan to mix the headspace. Air samples for CH_4 flux measurements were collected at 0 (chamber open), 5, 15 and 30 min in 60 ml polypropylene syringes fitted with gas-tight valves. Independent flux determinations were conducted in triplicate for each station during each sampling trip.

3.3 Pore water methane

Collection methods and pore water CH_4 data for Blaen Fign were reported previously in Bowes and Hornibrook (2006). The dissolved CH_4 abundances for Crymlyn Bog, Gors Lywd and Cors Caron are reported here for the first time. Briefly, the collection technique employed membrane-exchange equilibrators constructed of PVC that were installed ~15 cm from each ground collar. The equilibrators enabled sampling of pore water gases at closely spaced depth intervals (2 cm resolution) for measurement of dissolved CH_4 abundance. The design of Hesslein (1976) was modified to permit input and removal of de-ionised, de-gassed water after ground installation through 3-mm OD Tygon® tubes connected to 1×25×0.5 cm (H×W×D) troughs that were sealed with a gas and ion permeable membrane filter (0.2 μm pore size; HT-200, Pall Life Sciences).

3.4 Peat cores

Peat samples for porosity measurements and CH_4 oxidation kinetic experiments were obtained from monoliths (100 cm^2 cross-sectional area × 120 cm length) collected using a Wardenaar® peat corer (Eijelkamp, Netherlands). The peat was sectioned in the field into 1 dm^3 blocks, sealed in gas tight bags and then packed in ice for transport to the laboratory.

3.5 Soil temperature and water table level

Soil temperature was measured using an Omega Model HH-41 handheld thermistor thermometer and a thermistor probe. The latter consisted of a nylon-coated type-K thermocouple encased within a 5-cm long brass tube that had a wall thickness of 0.15 mm. The lead wire of the thermocouple was passed through a 2-m long stainless steel tube enabling the protected thermocouple tip to be inserted to specific depths in the peat soil. A nylon plug was used to isolate thermally the thermocouple tip from the stainless steel tube.

The ambient water-table level at each peatland was measured relative to the ground surface in a 10×10 cm hole that had been cut during a previous visit using the Wardenaar® corer.

3.6 Methane concentration analysis

Methane concentrations in air samples collected for determining flux rates were analyzed using a Carlo Erba HRGC5300 gas chromatograph (GC) equipped with gas-sampling valve (1 cm^3 sample loop), Porapak® QS packed column (3 mm×4 m), and flame ionization detector (FID). The carrier gas was helium at 35 ml min^{-1}, and FID support gases were hydrogen at 30 ml min^{-1} and zero air at 400 ml min^{-1}. Samples were injected through 1 cm^3 cartridges packed with magnesium perchlorate to remove H_2O. The relative precision of CH_4 analysis in air samples typically was better than ±2% based on replicate injections of BOC Specialty Gases alpha-gravimetric standards and actual samples. Flux rates were determined from the slope of linear regression equations fitted to the change in chamber CH_4 concentration versus time. Rates were corrected for the areal coverage and volume of the chambers, and are expressed in units of mg m^{-2} d^{-1}.

Methane was stripped from pore water into a headspace of helium using the method of McAullife (1971). The resulting gas samples were analyzed on the Carlo Erba

BGD
5, 2607–2643, 2008

HRGC5300 gas chromatograph (GC) under the same conditions used for analysis of CH_4 in flux samples. Pore water concentrations of CH_4 were corrected for differences in peat porosity and are expressed in units of μmol CH_4 l^{-1}.

3.7 Methane oxidation kinetics

Peat monoliths obtained from Cors Caron and Crymlyn Bog were subsampled in 5 cm slices (~0.5 dm^3) centred on five depths (5, 12.5, 20, 27.5 and 35 cm). The material was slurried in a 1:1 ratio with autoclaved de-ionised water. Slurry from each depth was incubated in triplicate at 15°C in crimp-top 35 ml Wheaton® serum vials containing a headspace of CH_4 in zero air corresponding to initial dissolved CH_4 concentrations (S_0) of ~10, 25, 50, 100, 250 and 500 μM. An additional slurry sample for each depth was incubated in singular as a blank containing a headspace of air only to confirm the absence of CH_4 production. Within two hours of loading the vial headspace, the actual value of S_0 in each vial was determined by GC-FID analysis of CH_4 in the headspace and Henry's Law. The rate of CH_4 oxidation was determined subsequently from the decrease in headspace concentration of CH_4 from time 0 (initial) to 24, 48 and 72 h. Gas samples were extracted using a 50 μl Hamilton® glass syringe fitted with a side-hole needle and gas-tight valve. Methane abundance was analyzed in triplicate using a Perkin Elmer® Clarus 500 gas chromatograph fitted with an Elite® PLOT Q mega-bore column (30 m × 0.53 mm diameter) and FID. The carrier gas was helium at 45 ml min^{-1} and FID support gases were hydrogen at 35 ml min^{-1} and zero air at 450 ml min^{-1}. The CH_4 oxidation rates determined independently in triplicate for each of the six S_0 values (i.e., 18 rate measurements per depth) were used to determine the maximum specific rate of CH_4 uptake (μ_m) and half saturation concentrations (K_s) for each depth interval in the two peatlands. Oxygen presumably was not a limiting factor in our experiments given that the incubations were conducted in zero air and hence the single Monod

BGD
5, 2607–2643, 2008

expression was used to describe methanotroph consumption of CH_4 in the vials:

$$\mu = \frac{\mu_m [CH_4]}{K_s + [CH_4]} \quad (1)$$

where μ is the rate of methanotrophy (μmol l^{-1} h^{-1}), μ_m is the maximum specific rate of CH_4 uptake (μmol l^{-1} h^{-1}), [CH_4] is the concentration of CH_4 (μmol l^{-1}) (i.e., S_0 values) and K_s is the concentration of CH_4 (μmol l^{-1}) required to attain half the maximum rate of CH_4 uptake. Equation (1) was fitted to the CH_4 oxidation rate and S_0 data using non-linear regression software (Prism v4.0, GraphPad Software, San Diego, CA, USA).

3.8 Diffusion rates for CH_4 in pore water

The rate of upward CH_4 diffusion in pore water at each peatland was determined using Fick's 1st Law:

$$J = D_S \left(\frac{d [CH_4]}{dz} \right) \quad (2)$$

where J is the flux rate (μmol cm^2 s^{-1}), D_s is the temperature and porosity corrected diffusion coefficient for CH_4 in water (cm^2 s^{-1}) and d[CH_4]/dz is the CH_4 concentration gradient (μmol cm^{-3} cm^{-1}) with depth (cm) in peat soils. Fick's 1st law was used because the amount of time required to sample an equilibrator profile (~1 h) is small and hence the measured gradients can be treated as being effectively steady state. Final values of J are expressed in mg CH_4 m^{-2} d^{-1} to facilitate comparison with CH_4 fluxes to the atmosphere measured using static chambers. The temperature dependency of D_S was based upon polynomial regression of diffusion coefficients for CH_4 in water in range 0 to 35°C (83rd Edition of the Handbook of Physics and Chemistry) which yielded the relationship:

$$D = 8.889 \times 10^{-11} T^3 - 1.714 \times 10^{-9} T^2 + 3.721 \times 10^{-7} T + 8.771 \times 10^{-6} \quad (3)$$

BGD
5, 2607–2643, 2008

A value of D was calculated for each CH_4 profile based upon the mean soil temperature measured in situ across the depth interval for which pore water CH_4 concentration data were linearly regressed to determine $d[CH_4]/dz$. Values of D were porosity corrected using Eq. (4) from Lerman (1979):

$$D_S = D\phi^2 \quad (4)$$

where ϕ is porosity (unitless). For each pore water data set, an average value of ϕ was calculated from in situ porosity measurements collected across the $d[CH_4]/dz$ depth interval.

4 Results

4.1 Daily precipitation and timing of sampling

The timing of sample collection at Crymlyn Bog, Cors Caron, Blaen Fign and Gors Lywd is shown in Fig. 2 in relation to total daily precipitation measured at UK Meteorological Office Stations (MOSs) situated near the peatlands. Swansea Victoria Park (Fig. 2a) and Swyddffynnon (Fig. 2b) MOSs are located immediately adjacent to Crymlyn Bog and Cors Caron, respectively, providing accurate daily precipitation records for each site. There are no active MOSs in close proximity to either Blaen Fign or Gors Lywd because of their remote locations in the Elan Valley. Consequently daily precipitation records from the Cwmystwyth and Llangurig MOSs, which geographically bracket the peatland sites, have been used (Fig. 2c and d)

4.2 Pore water CH_4

Pore water profiles of dissolved CH_4 measured in soils at the four peatlands during the summer of 2003 are shown in Figs. 3 to 6. Also shown in each figure panel is the ambient water table level at the time of sampling of the membrane equilibrators. The dashed line through the dissolved CH_4 data is a linear regression curve from which

$d[CH_4]/dz$ was obtained to calculate rates of upward CH_4 diffusion and the depth at which $[CH_4]=0\,\mu mol\,l^{-1}$ (i.e., the y-intercept denoted as $[CH_4]_0$). The gray horizontal bar delineates a 3 cm thick zone immediately beneath depth $[CH_4]_0$ in which potential rates of CH_4 oxidation were calculated based upon experimentally determined kinetic parameters (see Sect. 4.3) and in situ dissolved CH_4 concentrations. Where gaps existed in pore water $[CH_4]$ data, missing values were interpolated between adjacent CH_4 concentrations, including when necessary the point $[CH_4]_0=0\,\mu mol\,l^{-1}$.

Pore water CH_4 concentration profiles at all sites exhibited a similar shape although the size of the zone beneath the water table in which dissolved CH_4 abundance was below the detection limit of our analysis method varied widely between peatlands and sampling months at individual sites. The potential impact of the magnitude and timing of rainfall events on the size of the zone where $[CH_4]<0\,\mu mol\,l^{-1}$ will be explored further in Sect. 5.1.

4.3 CH_4 oxidation kinetics

Maximum potential rates of CH_4 oxidation (μ_m) and half saturation concentrations (K_s) determined from incubations of slurried peat are presented in Table 2. The methanotrophy rate and S_0 data were fitted twice with Eq. (1): once using all data (S_0=10 to 500 $\mu mol\,l^{-1}$) and a second time excluding the S_0=250 and 500 $\mu mol\,l^{-1}$ measurements (i.e., S_0=10 to 100 $\mu mol\,l^{-1}$). The μ_m and K_s values determined using all data are anomalous, in particular, the K_s values which exceed all half saturation constants reported to date for low affinity methanotropy by 1 to 2 orders of magnitude. The μ_m values are similarly high with values from the two samples in the depth interval 10 to 22.5 cm at Cors Caron being ~10 times greater than any maximum potential rates for CH_4 oxidation in freshwater environments reported to date. These anomalous values appear to result from the disproportionate effects of high CH_4 oxidation rates determined from the small number of incubations having S_0 values >100 $\mu mol\,l^{-1}$. Such concentrations of CH_4 are very rare in situ at the oxic-anoxic interface in peatlands

and consequently, Eq. (1) was fitted to the data a second time excluding CH_4 oxidation rates from the two highest values of S_0 (250 and 500 μmol l^{-1}). The resulting μ_m and K_s values are consistent with kinetic parameters typically associated for low affinity methanotrophy in aerobic environments. The half saturation concentrations are still amongst the highest reported to date; however, they are similar to published values of K_s for peat soils, which tend to be large relative to other methanotrophic environments (Segers, 1998).

Notably the S_0=10 to 100 μmol l^{-1} set of depth profiles of μ_m and K_s values do not show maxima at depths near the lower limit of water table fluctuations (which are present in the μ_m and K_s values from analysis of the complete data set). Instead μ_m values decrease steadily with increasing depth. The large standard errors associated with the K_s parameter preclude any broad generalisation about trends with depth of the half saturation constant in soils at either site.

4.4 Rates of CH_4 flux and consumption

A summary of rates of internal and external CH_4 fluxes (all sites) and subsurface methanotrophy potentials (Crymlyn Bog and Cors Caron only) are presented in Table 3. Rates of upward CH_4 flux into the methanotrophic zone were determined according to the method described in Sect. 3.8 and then scaled to a cross-sectional area of 1 m^2. The majority of CH_4 fluxes by pore water diffusion had a magnitude <10 mg m^{-2} d^{-1}. The concentration of dissolved CH_4 at the water table surface was >0 μmol l^{-1} in only 5 of the 33 pore water CH_4 profiles (Figs. 3c, e, g, 6c and f), suggesting that diffusion of CH_4 across the air-water interface contributes little to atmospheric emissions of CH_4 at these sites. Methane escaping from the water surface within the peat profile must still transit pore spaces and methanotroph populations in the unsaturated zone before reaching the atmosphere.

In all cases the rate of upward CH_4 flux was less than the capacity for CH_4 oxidation determined in a 3 cm thick zone immediately below the depth at which [CH_4]=0 μmol l^{-1}

BGD
5, 2607–2643, 2008

(Table 3). The potential for methanotrophy in the 3 cm thick zone was estimated by integrating rates of CH_4 oxidation calculated by substituting values of μ_m and K_s, and in situ dissolved CH_4 concentrations into Eq. (1). A peat interval of 3 cm downward from the point $[CH_4]_0$ was chosen because (i) depths above the point $[CH_4]_0$ yield methanotrophy rates (μ) equal to zero using Eq. (1), (ii) 3 cm was the minimum depth reported by Beckmann and Lloyd (2001) for penetration of O_2 by diffusion into a Scottish peat soil, and (iii) our aim was to provide a conservative estimate of CH_4 oxidation potentials based upon the kinetic parameters determined in laboratory incubations. For example, the values of potential capacity for CH_4 uptake noted in Table 3 (mg CH_4 m^{-2} d^{-1}) are ~3 orders of magnitude smaller than integrated oxidation rates reported by Sundh et al. (1994) for boreal peatlands in Sweden that were based upon a 0 to 60 cm depth interval (3.0 to 22.1 g CH_4 m^{-2} d^{-1}). Integration over large depth intervals is accurate when a double Monod expression incorporating availability of O_2 can be employed; however, we did not measure either in situ concentrations of pore water O_2 or kinetic parameters associated with O_2 consumption, hence we opted for the conservative approach of applying the determined μ_m and K_s values to a small depth interval in which O_2 was likely to be available.

The integrated methanotrophy potential rates were scaled to an area of 1 m^2 to facilitate comparison with pore water CH_4 diffusive fluxes and directly measured rates of CH_4 emission to the atmosphere. The latter also are shown in Table 3 and have been reported previously in Bowes and Hornibrook (2006) and Hornibrook and Bowes (2007). The CH_4 fluxes to the atmosphere are due only to steady-state diffusion processes (i.e., pore water or plant-mediated transport). Chamber measurements that exhibited erratic pulses (i.e., ebullition) were excluded from the flux analysis because it could not be determined conclusively whether the events were natural or induced during sample collection.

In the minerotrophic peatlands (Crymlyn Bog and Gors Lywd), CH_4 emission rates to the atmosphere typically exceeded maximum rates of CH_4 transport by pore water diffusion by one to two orders of magnitude, in particular, during summer months (Ta-

BGD
5, 2607–2643, 2008

ble 3). Fluxes of CH_4 to the atmosphere were much smaller from the ombrogenous peatlands (Blaen Fign and Cors Caron) with the exception of the sedge-rich plot (station 2) at Blaen Fign, consistent with the well known ability of many aquatic vascular flora to mediated gas transport via aerenchymatous tissue.

5 Discussion

5.1 The influence of precipitation events on pore water CH_4 profiles

Rates of both aerobic and anaerobic microbial processes in peat soils can be impacted by rainfall events through the introduction of electron acceptors such as O_2, SO_4^{2-} and NO_3^- (Dise and Verry, 2001; Gauci et al., 2002, 2004). Concentrations of microbial substrates in shallow peat layers, including dissolved gases (e.g., CH_4), also may be influenced through dilution which may affect rates of processes such as methanogenesis and methanotrophy (Kettunen et al., 1996). Thus the timing of CH_4 flux measurements or sampling of pore water CH_4 concentrations should be considered when possible in relation to short-term precipitation records.

The distance between the water table level and depth where $[CH_4]$=0 μmol l^{-1} (i.e., $[CH_4]_0$) differed greatly between the four peatland sites and sampling periods at individual sites (Figs. 3 to 6). The potential influence of precipation input on this parameter was explored by comparing the depth to $[CH_4]_0$ in the saturated zone with rainfall amounts on (i) the day of sampling, and (ii) the periods 1, 3, 5 and 7 days before sampling of pore water. Significant correlations existed with cumulative rainfall during the period 3 days prior to pore water sampling (Fig. 7 and Table 4) but not the amount of rainfall over shorter or longer periods before sample collection (data not shown; r^2 values typically <0.40). A few of the weaker correlations in Fig. 7 (e.g., Cors Caron, stations 1 and 2) result from single data points heavily skewing the linear regression analysis because of the small size of the data sets (i.e., typically n=4). Regression lines have a negative slope only for Crymlyn Bog, the most minerotrophic of the peatlands

BGD
5, 2607–2643, 2008

which receives significant moisture input from groundwater as well as precipitation. For the other three peatlands, including Gors Lywd which is positioned at the head of a small catchment, the slopes of the regression equations are positive. The analysis in Table 4 and Fig. 7 suggests that in the absence of significant rainfall events, the depth of $[CH_4]_0$ is not as variable as implied in Figs. 3 to 6. The large range of values for this parameter likely reflect differences in recent input of precipitation rather than microbiological driven changes in methane production and consumption. The "normal" depth of $[CH_4]_0$ appears to vary between individual peatlands as indicated by differences in the y-intercepts of the regression equations in Table 4 (e.g., ~10 cm for Gors Lywd versus ~5 cm for Blaen Fign).

Noteworthy in Fig. 7 are the infilled data points for Cors Caron and Crymlyn Bog that lie largely at x-values of ~0 mm (i.e., when little or no rainfall occurred prior to the sampling period). The infilled points (5 in total) represent times when the concentration of dissolved CH_4 at the water table level exceeded 0 μmol l^{-1} and CH_4 transport was occurring across the subsurface air-water interface. The correlations in Table 4 will be unimportant during periods of low rainfall and at those times CH_4 most likely is able to diffuse across the water table surface because heterotrophic activity in the unsaturated zone has depleting O_2 from pore spaces.

5.2 CH_4 oxidation kinetics

The μ_m values determined for different depth intervals at Crymlyn Bog and Cors Caron (Table 3; S_0=10 to 100 μmol l^{-1} values) lie within the range of potential methane oxidation rates (0.1 to 100 μmol m^{-3} s^{-1}) compiled by Segers (1998) for different types of environments that host low affinity methanotrophic activity. Conversion of units in Table 3 for comparison yield μ values of 0.5 to 1.1 and 2.9 to 5.9 μmol m^{-3} s^{-1}, respectively, for Crymlyn Bog and Cors Caron. Half saturation constants for Cors Caron also are higher than values for Crymlyn Bog. It is unclear why methanotrophs in the raised bog environment should have a lower affinity for substrate (i.e., higher K_s) and molecular bi-

ology data are unavailable to determine whether differences existed in methanotrophic communities at the two peatlands. Although the two peatlands differ in the composition and pH of their soil solution, we cannot speculate about potential relationships between the parameters μ_m and K_s, and factors such as pH because slurries were diluted 1:1 with deionized water. The buffering capacity of peat from the two sites would have differed considerably (i.e., rainfed versus groundwater influenced). However, K_s values cited by Segers (1997) for peat soil ranged from 1 to 45 μmol l^{-1}, encompassing the values determined for Crymlyn Bog. Watson et al. (1997) reported a K_s of 57.9 μmol l^{-1} for CH_4 oxidation in acidic peat from Ellergower Moss, comparable to the range of half saturation constants determined with depth for Cors Caron, which also is a raised bog (i.e., 42.6 to 68.1 μmol l^{-1}; Table 3).

The ranges of μ_m and K_s values in Table 3 are noteworthy also because of the difficulties such variability presents in efforts to model CH_4 dynamics in peatland soils. For example, one of the more rigorous process-based models for estimating CH_4 flux from peatlands (Walter and Heimann, 2000) employs the assumption that the parameters μ_m and K_s for methanotrophy are constant with depth and in different types of wetlands, assigning values of 20 μmol l^{-1} h^{-1} and 5 μmol l^{-1}, respectively. The mean μ_m values for Crymlyn Bog and Cor Caron suggest that maximum rates of CH_4 oxidation may differ between minerotrophic and ombrogenous mires and in both cases appear to decrease gradually with depth. As noted previously, half saturation concentrations also may be higher in acidic rainfed peatlands (e.g., Table 3 and Watson et al., 1997). Availability of kinetic parameters describing CH_4 oxidation in peatlands is too limited at present to attempt to develop generalised relationships describing μ_m and K_s in different types of peatlands and spatially and temporally within individual sites.

5.3 Methane supply, demand and net flux

The amount of upward CH_4 transport in all four peatlands via pore water diffusion typically was <10 mg m^{-2} d^{-1} and exceeded this value in only 4 of the 33 pore water CH_4

profiles collected during the summer of 2003. Rates of CH_4 emission to the atmosphere from Blaen Fign and Cors Caron were the same order of magnitude as pore water CH_4 diffusion rates; however, it is unlikely that CH_4 transport by this mode contributed to atmospheric flux. The stable carbon isotope compositions ($\delta^{13}C$ values) of CH_4 in pore water and surface flux have been used previously to demonstrate that emission of CH_4 to the atmosphere at all four peatlands occurs predominately via plant-mediated transport (Bowes and Hornibrook, 2006; Hornibrook and Bowes, 2007). For example, CH_4 emitted at a higher rate from sedge-rich station 2 at Blaen Fign has $\delta^{13}C$ values that are statistically indistinguishable from CH_4 emissions from *Sphagnum*-rich station 1 (Bowes and Hornibrook, 2006). The $\delta^{13}C$ composition of CH_4 emissions from both plots are ^{13}C-depleted by ~15 to 20‰ relative to pore water CH_4, which eliminates the possibility that the small quantities of CH_4 emitted from station 1 is residual CH_4 that has survived transit across the unsaturated zone (Happell et al., 1994; Popp et al., 1999). Similarly, CH_4 emissions from Cors Caron, Crymlyn Bog and Gors Lywd also are ^{13}C-depleted relative to the pore water CH_4 pool (Hornibrook and Bowes, 2007). These conclusions about transport processes based upon stable isotope data are consistent with the observation reported here that low affinity methanotrophs in the 3 cm thick zone where CH_4 first appears in the pore water pool (i.e., immediately below the depth $[CH_4]_0$) have a capacity for CH_4 consumption that significantly exceeds the upward CH_4 supply via pore water diffusion (Table 3). While low affinity methanotrophs appear to consume the bulk of CH_4 transported along concentration gradients in pore water, they do not provide a robust barrier to CH_4 flux from peatlands because of the prevalence of CH_4 movement through vascular flora which bypasses the methanotrophy filter. During June to August, microbial CH_4 oxidation rates ranged from 0.8 to 40.7% of total CH_4 flux to the atmosphere in Crymlyn Bog and Gors Lywd; however, the majority of values were <10%. In the same months, the percentages were higher at sedge-poor plots at the ombrogeneous mires (Blaen Fign, ~9.3 to 53.4%; Cors Caron, 11.0 to 21.1%), but the difference in proportions is unimportant because as indicated by $\delta^{13}C$ data little or none of the diffusion transported CH_4 contributed to

BGD
5, 2607–2643, 2008

surficial emissions (Hornibrook and Bowes, 2007). Consequently, in the absence of bacterial CH_4 oxidation the CH_4 flux rate from minerotrophic peatlands would not be significantly greater in absolute terms but the increase would be proportionally much larger in ombrogenous bogs. The steady state flux rates of >100 mg CH_4 m^{-2} d^{-1} commonly observed from wetland soils (e.g., Whalen, 2005) would be difficult to achieve if pore water diffusion alone was the dominant transport mechanism of CH_4. The bulk of CH_4 emitted from peatlands typically occurs via vascular flora and possibly ebullition, although data for the latter transport process remain sparse (Baird et al., 2004).

6 Conclusions

The depth below ambient water table levels at which dissolved methane is depleted to a concentration of ~0 μmol l^{-1} by methanotrophic activity varied widely between peatlands and temporally within individual peatlands. Short-term precipitation events appeared to increase the depth to $[CH_4]_0$ without necessarily disturbing dissolved CH_4 profiles. In the absence of recent rainfall input, the depth of $[CH_4]_0$ below the water table level ranged from ~5 to 10 cm, although the size of the interval diminished to 0 (i.e., CH_4 present at the water table surface) during prolonged periods without precipitation input.

The capacity for methanotrophy in peatland soils from both minerotrophic and ombrogenous peatlands typically was greater than the available supply of upward diffusing CH_4. Kinetic parameters (μ_m and K_s) describing the response of methanotroph populations to substrate (i.e., CH_4) concentrations are not constant with depth as assumed in some process models and both parameters were larger in the ombrogenous versus minerotrophic peatlands. Low affinity methanotrophic activity effectively consumes the majority of upward diffusing CH_4 in peatland soil (in most cases 100%); however, in the absence of bacterial CH_4 oxidation the flux rate from minerotrophic peatlands would not be significantly greater. Maximum rates of CH_4 flux by pore water diffusion were at most 10 to 20 mg m^{-2} d^{-1}, which in minerotrophic mires represents typically <10% of

BGD
5, 2607–2643, 2008

actual emissions. The generally lower CH_4 emission rates from ombrogeneous mires would be impacted more by cessation or attentuation of methanotrophy activity but CH_4 flux rates would still amount to only a few 10 s of mg m^{-2} d^{-1}.

Acknowledgements. We thank Mike Dury for manufacturing flux chambers and pore water equilibrators. HLB was supported by an NERC postgraduate scholarship and AVGS by a NERC Industrial CASE scholarship. This study was funded by NERC (NER/B/S/2000/00076) and Royal Society (574006.G503/21832/SM) grants to ERCH. The UK Joint Higher Education Funding Council for England and Office of Science and Technology Science Research Investment Fund (SRIF), and the University of Bristol are thanked for infrastructure funding. We thank the British Atmospheric Data Centre (BADC) for technical advice and permission to use daily precipitation data from Met Office weather stations in Wales.

References

Baird, A. J., Beckwith, C. W., Waldron, S., and Waddington, J. M.: Ebullition of methane-containing gas bubbles from near-surface sphagnum peat, Geophys. Res. Lett., 31, L21505, doi:10.1029/2004GL021157, 2004.

Basiliko, N., Blodau, C., Roehm, C., Bengtson, P., and Moore, T. R.: Regulation of decomposition and methane dynamics across natural, commercially mined, and restored northern peatlands, Ecosystems, 10, 1148–1165, 2007.

Beckmann, M. and Lloyd, D.: Mass spectrometric monitoring of gases (CO_2, CH_4, O_2) in a mesotrophic peat core from Kopparas Mire, Sweden, Global Change Biol., 7, 171–180, 2001.

Berestovskaya, Y. Y., Rusanov, I. I., Vasil'eva, L. V., and Pimenov, N. V.: The processes of methane production and oxidation in the soils of the Russian arctic tundra, Microbiology, 74, 221–229, 2005.

Boon, P. I. and Lee, K.: Methane oxidation in sediments of a floodplain wetland in south-eastern australia, Lett. Appl. Microbiol., 25, 138–142, 1997.

Bowes, H. L. and Hornibrook, E. R. C.: Emision of highly ^{13}C-depleted methane from an upland blanket mire, Geophys. Res. Lett., 33, L04401, doi:10.1029/2005GL025209, 2006.

Calhoun, A. and King, G. M.: Characterization of root-associated methanotrophs from three

freshwater macrophytes: Pontederia cordata, Sparganium eurycarpum, and Sagittaria latifolia, Appl. Environ. Microb., 64, 1099–1105, 1998.
Chen, Y., Dumont, M. G., McNamara, N. P., Chamberlain, P. M., Bodrossy, L., Stralis-Pavese, N., and Murrell, J. C.: Diversity of the active methanotrophic community in acidic peatlands as assessed by mRNA and SIP-PLFA analyses, Environ. Microbiol., 10, 446–459, 2008.
Dedysh, S. N.: Methanotrophic bacteria of acidic sphagnum peat bogs, Microbiology, 71, 638–650, 2002.
Dedysh, S. N., Derakshani, M., and Liesack, W.: Detection and enumeration of methanotrophs in acidic sphagnum peat by 16s rRNA fluorescence in situ hybridization, including the use of newly developed oligonucleotide probes for Methylocella palustris, Appl. Environ. Microb., 67, 4850–4857, 2001.
Dedysh, S. N., Dunfield, P. F., Derakshani, M., Stubner, S., Heyer, J., and Liesack, W.: Differential detection of type II methanotrophic bacteria in acidic peatlands using newly developed 16s rRNA-targeted fluorescent oligonucleotide probes, FEMS Microbiol. Ecol., 43, 299–308, 2003.
Dise, N. B. and Verry, E. S.: Suppression of peatland methane emission by cumulative sulfate deposition in simulated acid rain, Biogeochemistry, 53, 143–160, 2001.
Edwards, C., Hales, B. A., Hall, G. H., McDonald, I. R., Murrell, J. C., Pickup, R., Ritchie, D. A., Saunders, J. R., Simon, B. M., and Upton, M.: Microbiological processes in the terrestrial carbon cycle: Methane cycling in peat, Atmos. Environ., 32, 3247–3255, 1998.
Gauci, V., Dise, N., and Fowler, D.: Controls on suppression of methane flux from a peat bog subjected to simulated acid rain sulfate deposition, Global Biogeochem. Cy., 16, 1004, doi:10.1029/2000GB001370, 2002.
Gauci, V., Matthews, E., Dise, N., Walter, B., Koch, D., Granberg, G., and Vile, M.: Sulfur pollution suppression of the wetland methane source in the 20th and 21st centuries, P. Natl. Acad. Sci. USA, 101, 12 583–12 587, 2004.
Gutknecht, J. L. M.: Linking soil process and microbial ecology in freshwater wetland ecosystems, Plant Soil, 289, 17–34, 2006.
Happell, J. D., Chanton, J. P., and Showers, W. S.: The influence of methane oxidation on the stable isotopic composition of methane emitted from florida swamp forests, Geochim. Cosmochim. Ac., 58, 4377–4388, 1994.
Hesslein, R. H.: An in situ sampler for close interval pore water studies, Limnol. Oceanogr., 21(6), 912–914, 1976.

Hornibrook, E. R. C. and Bowes, H. L.: Trophic status impacts both the magnitude and stable carbon isotope composition of methane flux from peatlands, Geophys. Res. Lett., 34, L21401, doi:10.1029/2007GL031231, 2007.
Joabsson, A. and Christensen, T. R.: Methane emissions from wetlands and their relationship with vascular plants: An arctic example, Global Change Biol., 7, 919–932, 2001.
Joabsson, A., Christensen, T. R., and Wallen, B.: Vascular plant controls on methane emissions from northern peatforming wetlands, Trends Ecol. Evol., 14, 385–388, 1999.
Kettunen, A.: Connecting methane fluxes to vegetation cover and water table fluctuations at microsite level: A modeling study, Global Biogeochem. Cy., 17, 1051, doi:10.1029/2002GB001958, 2003.
Kettunen, A., Kaitala, V., Alm, J., Silvola, J., Nykanen, H., and Martikainen, P. J.: Cross-correlation analysis of the dynamics of methane emissions from a boreal peatland, Global Biogeochem. Cy., 10, 457–471, 1996.
Kettunen, A., Kaitala, V., Lehtinen, A., Lohila, A., Alm, J., Silvola, J., and Martikainen, P. J.: Methane production and oxidation potentials in relation to water table fluctuations in two boreal mires, Soil Biol. Biochem., 31, 1741–1749, 1999.
King, G. M.: Dynamics and controls of methane oxidation in a danish wetland sediment, FEMS Microbiol. Ecol., 74, 309–323, 1990.
King, G. M.: Associations of methanotrophs with the roots and rhizomes of aquatic vegetation, Appl. Environ. Microb., 60, 3220–3227, 1994.
King, G. M.: In situ analyses of methane oxidation associated with the roots and rhizomes of a bur reed, sparganium eurycarpum, in a maine wetland, Appl. Environ. Microb., 62, 4548–4555, 1996.
Kreuzer-Martin, H. W.: Stable isotope probing: Linking functional activity to specific members of microbial communities, Soil Sci. Soc. Am. J., 71, 611–619, 2007.
Krumholz, L. R., Hollenback, J. L., Roskes, S. J., and Ringelberg, D. B.: Methanogenesis and methanotrophy within a sphagnum peatland, FEMS Microbiol. Ecol., 18, 215–224, 1995.
Le Mer, J. and Roger, P.: Production, oxidation, emission and consumption of methane by soils: A review, Eur. J. Soil Biol., 37, 25–50, 2001.
Lerman, A.: Geochemical processes: Water and sediment environments, John Wiley & Sons, New York, 481 pp., 1979.
McAullife, C.: GC determination of solutes by multiple phase equilibration, Chem. Technol., 1, 46–51, 1971.

McDonald, I. R., Hall, G. H., Pickup, R. W., and Murrell, J. C.: Methane oxidation potential and preliminary analysis of methanotrophs in blanket bog peat using molecular ecology techniques, FEMS Microbiol. Ecol., 21, 197–211, 1996.
McDonald, I. R., Upton, M., Hall, G., Pickup, R. W., Edwards, C., Saunders, J. R., Ritchie, D. A., and Murrell, J. C.: Molecular ecological analysis of methanogens and methanotrophs in blanket bog peat, Microb. Ecol., 38, 225–233, 1999.
McDonald, I. R., Radajewski, S., and Murrell, J. C.: Stable isotope probing of nucleic acids in methanotrophs and methylotrophs: A review, Org. Geochem., 36, 779–787, 2005.
Megonigal, J. P. and Schlesinger, W. H.: Methane-limited methanotrophy in tidal freshwater swamps, Global Biogeochem. Cy., 16, 1088, doi:10.1029/2001GB001594, 2002.
Mikaloff Fletcher, S. E., Tans, P. P., Bruhwiler, L. M., Miller, J. B., and Heimann, M.: CH_4 sources estimated from atmospheric observations of CH_4 and its $^{13}C/^{12}C$ isotopic ratios: 2. Inverse modeling of CH_4 fluxes from geographical regions, Global Biogeochem. Cy., 18, GB4005, doi:10.1029/2004GB002224, 2004.
Mikkelä, C., Sundh, I., Svensson, B. H., and Nilsson, M.: Diurnal variation in methane emission in relation to the water-table, soil temperature, climate and vegetation cover in a swedish acid mire, Biogeochemistry, 28, 93–114, 1995.
Miller, D. N., Yavitt, J. B., Madsen, E. L., and Ghiorse, W. C.: Methanotrophic activity, abundance, and diversity in forested swamp pools: Spatiotemporal dynamics and influences on methane fluxes, Geomicrobiol. J., 21, 257–271, 2004.
Morris, S. A., Radajewski, S., Willison, T. W., and Murrell, J. C.: Identification of the functionally active methanotroph population in a peat soil microcosm by stable-isotope probing, Appl. Environ. Microb., 68, 1446–1453, 2002.
Oquist, M. G. and Svensson, B. H.: Vascular plants as regulators of methane emissions from a subarctic mire ecosystem, J. Geophys. Res., 107, 4580, doi:10.1029/2001JD001030, 2002.
Pearce, D. M. E., and Clymo, R. S.: Methane oxidation in a peatland core, Global Biogeochem. Cy., 15, 709-720, 2001.
Popp, T. J., Chanton, J. P., Whiting, G. J., and Grant, N.: Methane stable isotope distribution at a carex dominated fen in north central alberta, Global Biogeochem. Cy., 13, 1063–1077, 1999.
Popp, T. J., Chanton, J. P., Whiting, G. J., and Grant, N.: Evaluation of methane oxidation in the rhizosphere of a carex dominated fen in north central alberta, canada, Biogeochemistry, 51, 259–281, 2000.

Ritchie, D. A., Edwards, C., McDonald, I. R., and Murrell, J. C.: Detection of methanogens and methanotrophs in natural environments, Global Change Biol., 3, 339–350, 1997.
Roslev, P. and King, G. M.: Regulation of methane oxidation in a freshwater wetland by water table changes and anoxia, FEMS Microbiol. Ecol., 19, 105–115, 1996.
Roulet, N. T., Ash, R., Quinton, W., and Moore, T.: Methane flux from drained northern peatlands: Effect of a persistent water table lowering on flux, Global Biogeochem. Cy., 7, 749–769, 1993.
Schipper, L. A. and Reddy, K. R.: Determination of methane oxidation in the rhizosphere of Sagittaria lancifolia using methyl fluoride, Soil Sci. Soc. Am. J., 60, 611–616, 1996.
Segers, R.: Methane production and methane consumption: A review of processes underlying wetland methane fluxes, Biogeochemistry, 41, 23–51, 1998.
Shannon, R. D., White, J. R., Lawson, J. E., and Gilmour, B. S.: Methane efflux from emergent vegetation in peatlands, J. Ecol., 84, 239–246, 1996.
Ström, L. and Christensen, T. R.: Below ground carbon turnover and greenhouse gas exchanges in a sub-arctic wetland, Soil Biol. Biochem., 39, 1689–1698, 2007.
Ström, L., Mastepanov, M., and Christensen, T. R.: Species-specific effects of vascular plants on carbon turnover and methane emissions from wetlands, Biogeochemistry, 75, 65–82, 2005.
Sundh, I., Nilsson, M., Granberg, G., and Svensson, B. H.: Depth distribution of microbial production and oxidation of methane in northern boreal peatlands, Microb. Ecol., 27, 253–265, 1994.
Sundh, I., Borga, P., Nilsson, M., and Svensson, B. H.: Estimation of cell numbers of methanotrophic bacteria in boreal peatlands based on analysis of specific phospholipid fatty acids, FEMS Microbiol. Ecol., 18, 103–112, 1995.
Sundh, I., Nilsson, M., and Borga, P.: Variation in microbial community structure in two boreal peatlands as determined by analysis of phospholipid fatty acid profiles, Appl. Environ. Microb., 63, 1476–1482, 1997.
Tokida, T., Miyazaki, T., Mizoguchi, M., Nagata, O., Takakai, F., Kagemoto, A., and Hatano, R.: Falling atmospheric pressure as a trigger for methane ebullition from peatland, Global Biogeochem. Cy., 21, GB2003, doi:10.1029/2006GB002790, 2007a.
Tokida, T., Mizoguchi, M., Miyazaki, T., Kagemoto, A., Nagata, O., and Hatano, R.: Episodic release of methane bubbles from peatland during spring thaw, Chemosphere, 70, 165–171, 2007b.

van der Nat, F. J. W. A. and Middelburg, J. J.: Seasonal variation in methane oxidation by the rhizosphere of phragmites australis and scirpus lacustris, Aquat. Bot., 61, 95–110, 1998.
Walter, B. P., Heimann, M., and Matthews, E.: Modeling modern methane emissions from natural wetlands 1. Model description and results, J. Geophys. Res., 106, 34 189–34 206, 2001.
Wartiainen, I., Hestnes, A. G., and Svenning, M. M.: Methanotrophic diversity in high arctic wetlands on the islands of Svalbard (Norway) – denaturing gradient gel electrophoresis analysis of soil DNA and enrichment cultures, Can. J. Microbiol., 49, 602–612, 2003.
Watson, A., Stephen, K. D., Nedwell, D. B., and Arah, J. R. M.: Oxidation of methane in peat: Kinetics of CH_4 and O_2 removal and the role of plant roots, Soil Biol. Biochem., 29, 1257–1267, 1997.
Whalen, S. C.: Biogeochemistry of methane exchange between natural wetlands and the atmosphere, Environ. Eng. Sci., 22, 73–94, 2005.
Whalen, S. C. and Reeburgh, W. S.: Methane oxidation, production, and emission at contrasting sites in a boreal bog, Geomicrobiol. J., 17, 237–251, 2000.

Table 1. Sites, wetland types, locations and pore water pH (Hornibrook and Bowes, 2007).

Site	Wetland Type	Latitude	Longitude	Altitude (m a.s.l.)[a]	pH[b]
Crymlyn Bog	intermediate fen	51°38′11″ N	03°53′18″ W	9	5.5±0.5 (n=20)
Gors Lywd	upland valley mire	52°15′44″ N	03°34′44″ W	385	4.9±0.6 (n=20)
Blaen Fign	blanket bog	52°15′44″ N	03°34′44″ W	504	4.2±0.3 (n=20)
Cors Caron	raised bog	52°15′24″ N	03°55′00″ W	160	4.2±0.1 (n=20)

[a] m a.s.l. = meters above sea level
[b] Mean pore water pH ± standard deviation (1σ; n=# of measurements) from 5 to 45 cm depth for May to August 2003.

BGD
5, 2607–2643, 2008

Table 2. Maximum CH_4 oxidation rates (μ_m) and half saturation constants (K_s).

Site	Depth Interval cm	S_0=10 to 500 μmol l^{-1} μ_m±SE[a] μmol l^{-1} h^{-1}	S_0=10 to 500 μmol l^{-1} K_s±SE[a] μmol l^{-1}	S_0=10 to 100 μmol l^{-1} μ_m±SE[a] μmol l^{-1} h^{-1}	S_0=10 to 100 μmol l^{-1} K_s±SE[a] μmol l^{-1}
Crymlyn Bog	2.5 to 7.5	26±8	231±116	4.1±0.9	8.3±8.0
	10 to 15	70±78	903±1329	dnc[b]	dnc[b]
	17.5 to 22.5	40±19	198±187	3.3±1.9	10.2±20.1
	25 to 30	8±2	137±93	1.8±1.8	11.5±40.0
	32.5 to 37.5	dnc[b]	dnc[b]	dnc[b]	dnc[b]
Cors Caron	2.5 to 7.5	24±3	83±30	21.1±6.4	68.1±38.0
	10 to 15	103±97	881±1091	15.6±3.9	45.8±25.1
	17.5 to 22.5	106±88	956±1026	14.5±4.0	51.2±28.6
	25 to 30	43±17	353±208	10.5±1.9	42.6±17.1
	32.5 to 37.5	25±8	54±49	dnc[b]	dnc[b]

[a] SE = standard error
[b] dnc = did not converge

Table 3. Internal and external methane fluxes and subsurface oxidation potentials.

Site and Date	Station 1[a]			Station 2[a]		
	CH_4 flux into oxidation zone[b] mg CH_4 m^{-2} d^{-1}	Potential CH_4 oxidation rate[c] mg CH_4 m^{-2} d^{-1}	Surface CH_4 flux[d] mg CH_4 m^{-2} d^{-1}	CH_4 flux into oxidation zone[b] mg CH_4 m^{-2} d^{-1}	Potential CH_4 oxidation rate[c] mg CH_4 m^{-2} d^{-1}	Surface CH_4 flux[d] mg CH_4 m^{-2} d^{-1}
Crymlyn Bog						
27 May 2003	4.4±0.2	35.2	26.3±16.4			156±68
2 Jul 2003	15.8±5.7	30.7	42.6±22.6	9.3±0.9[e]	9.6	130±16
28 Jul 2003	1.6±0.1	26.7	52.4±17.6	2.4±0.3[e]	20.8	279±27
19 Aug 2003	3.4±0.4	18.8	116±62	2.4±0.3[e]	30.0	287±116
Gors Lywd						
19 May 2003	2.9±0.3	–	4.7±2.0	4.4±0.3	–	2.3±1.1
24 Jun 2003	17.6±2.8	–	–	13.7±0.0	–	33.6±9.8
23 Jul 2003	17.5±0.0	–	461±99	6.1±1.1	–	168
11 Aug 2003	7.7±1.2	–	872	5.4±2.5	–	386±251
Blaen Fign						
30 Apr 2003	5.6±0.8	–	–0.8±0.7	1.9±0.2	–	36.4±27.5
4 Jun 2003	2.5±0.3	–	17.9±2.4	6.1±1.1	–	187±30
8 Jul 2003	3.9±1.0	–	7.3±5.2	3.4±0.1	–	73.5±77.8
5 Aug 2003	1.3±0.4	–	10.5±2.2	3.1±0.0	–	85.4±58.6
2 Sep 2003	2.0±0.3	–	21.4±12.5	3.6±0.4	–	99.4±16.7
Cors Caron						
7 May 2003	5.3±1.3	59.3	4.8±2.4	8.1±0.8	63.4	0.3±0.1
17 Jun 2003	1.5±0.1[e]	35.6	8.8±3.2	1.4±0.0	34.5	12.2±2.4
14 Jul 2003	2.3±0.6	15.1	11.8±4.2	1.3±0.4[e]	5.3	10.1±3.6
25 Aug 2003	2.0±0.2	34.9	18.2±7.7	2.7±0.5	32.3	12.8±4.3

[a] The ground surface at station 1 contained a greater abundance of *Sphagnum* and fewer vascular species than station 2 at Crymlyn Bog and Blaen Fign.

[b] Rates of internal CH_4 flux into the zone of methanotrophy based upon Fick's 1st law (Eq. 2) and linear regression analysis of pore water CH_4 data shown in Figs. 2 to 5.

[c] Potential rate of CH_4 oxidation in a 3 cm thick zone below the depth at which $[CH_4]=0\,\mu mol\,l^{-1}$ defined by the y-intercept of linear regression analysis of pore water CH_4 concentration data in Figs. 2 to 5. The total potential rate of CH_4 oxidation in the 3 cm thick zone is based upon actual CH_4 concentrations measured in peat soils and the depth distribution of μ_m and K_s parameters determined experimentally for Crymlyn Bog and Cors Caron (Table 2).

[d] Total diffusive CH_4 flux to the atmosphere measured using closed dynamic chambers and reported previously in Bowes and Hornibrook (2006) and Hornibrook and Bowes (2007).

[e] The concentration of dissolved CH_4 in pore water at the subsurface air-water interface was $>0\,\mu mol\,l^{-1}$ on these days.

BGD

5, 2607–2643, 2008

Table 4. Equations for linear regression curves in Fig. 7.

Site	Station 1	Station 2
Crymlyn Bog	y = −0.41 x + 5.13 (r^2=0.98)	y = −0.22 x − 2.95 (r^2=0.29)
Gors Lywd	y = 0.86 x + 9.17 (r^2=0.94)	y = 0.68 x + 11.05 (r^2=0.81)
Blaen Fign	y = 0.74 x + 5.45 (r^2=0.91)	y = 0.62 x + 4.77 (r^2=0.40)
Cors Caron	y = 2.03 x − 0.29 (r^2=0.61)[a]	y = 0.71 x + 5.06 (r^2=0.07)[b]

[a] Exclusion of 17 June 2003 data point yields y=1.61+3.01 (r^2=0.84).
[b] Exclusion of the 25 August 2003 data point yields y=1.61−1.29 (r^2=0.99).

BGD
5, 2607–2643, 2008

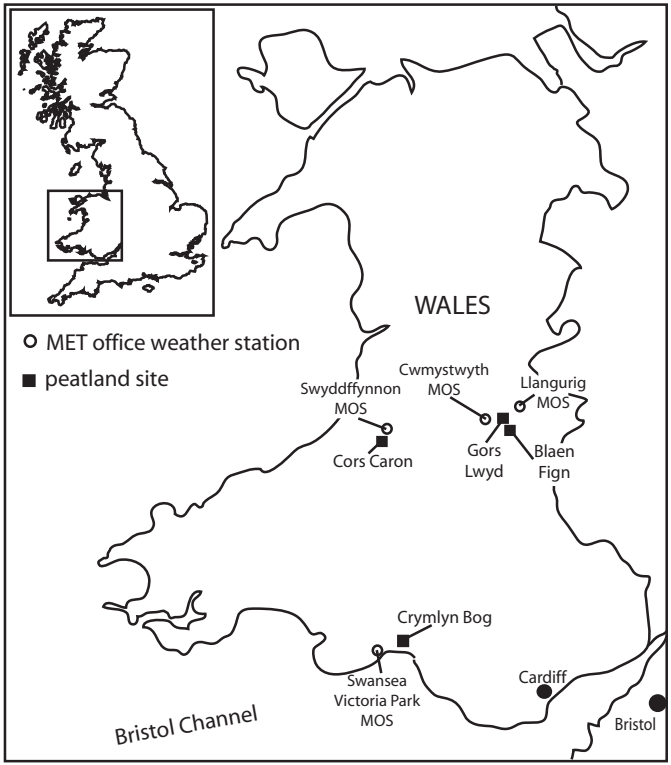

Fig. 1. Locations of peatland study sites and Met Office MIDAS Land Surface Observation Stations (MOS = Met Office Station) in Wales, UK. Details of the four peatlands are provided in Table 1, including map coordinates.

BGD
5, 2607–2643, 2008

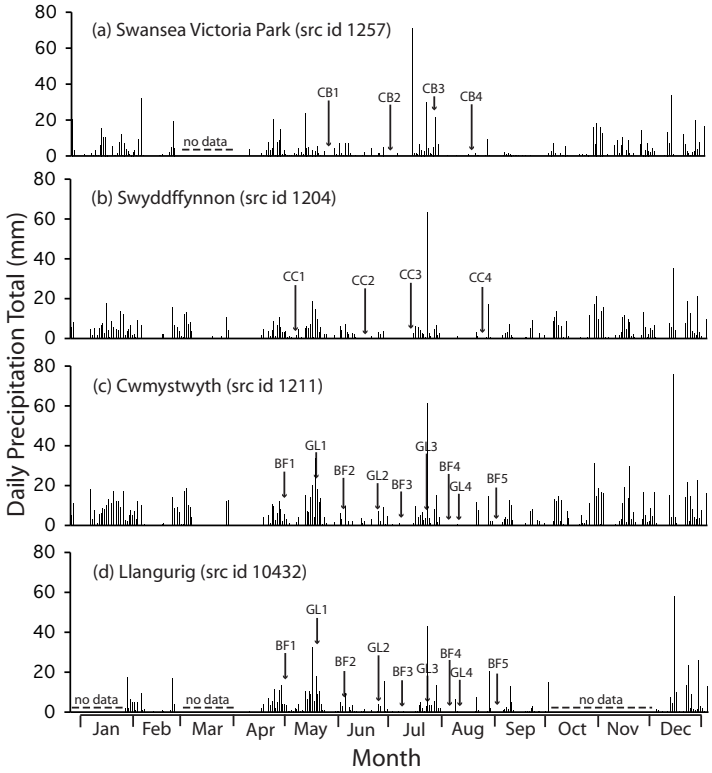

Fig. 2. Sample collection dates at Crymlyn Bog (CB1 27.5.03; CB2 2.7.03; CB3 28.7.03; CB4 19.8.03), Cors Caron (CC1 7.5.03; CC2 17.6.03; CC3 14.7.03; CC4 25.8.03), Blaen Fign (BF1 30.4.03; BF2 4.6.03; BF3 8.7.03; BF4 5.8.03; BF5 2.9.03), and Gors Lywd (GL1 19.5.03; GL2 24.6.03; GL3 23.7.03; GL4 11.8.03) and daily precipitation amounts for 2003 from Met Office MIDAS Land Surface Observation Stations at Swansea Victoria Park (src id 1257; 51°36′43″ N, 03°57′43″ W; 8 m a.s.l.), Swyddffynnon (src id 1204; 52°16′19″ N, 03°54′54″ W; 168 m a.s.l.), Cwmystwyth (src id 1211; 52°21′29″ N, 03°48′07″ W; 301 m a.s.l.), and Llangurig (src id 10432; 52°24′14″ N, 03°36′22″ W; 273 m a.s.l.).

BGD
5, 2607–2643, 2008

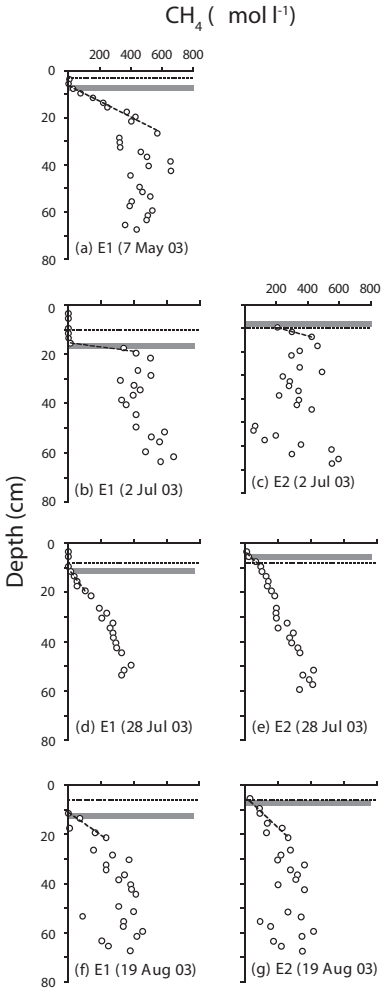

Fig. 3. Pore water profiles of dissolved CH_4 measured at Crymlyn Bog during the summer of 2003 from pore water equilibrators E1 and E2. Water-table level in each panel is indicated by a dotted horizontal line. The dashed line through shallow CH_4 values trending to zero concentration is a regression line fitted to the data to determine the gradient $d[CH_4]/dz$, which was used to calculate rates of CH_4 flux into the methanotrophic zone.

BGD
5, 2607–2643, 2008

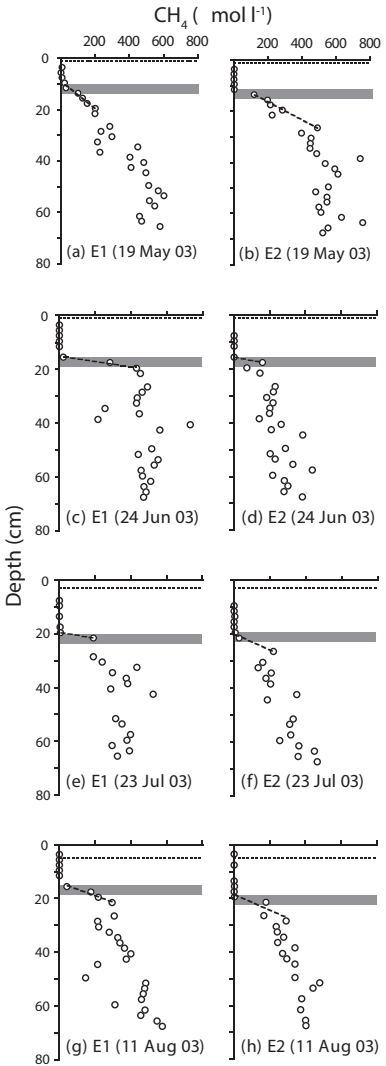

Fig. 4. Pore water profiles of dissolved CH_4 measured at Gors Lywd during the summer of 2003 from pore water equilibrators E1 and E2. Water-table level in each panel is indicated by a dotted horizontal line. The dashed line through shallow CH_4 values trending to zero concentration is a regression line fitted to the data to determine the gradient $d[CH_4]/dz$, which was used to calculate rates of CH_4 flux into the methanotrophic zone.

BGD
5, 2607–2643, 2008

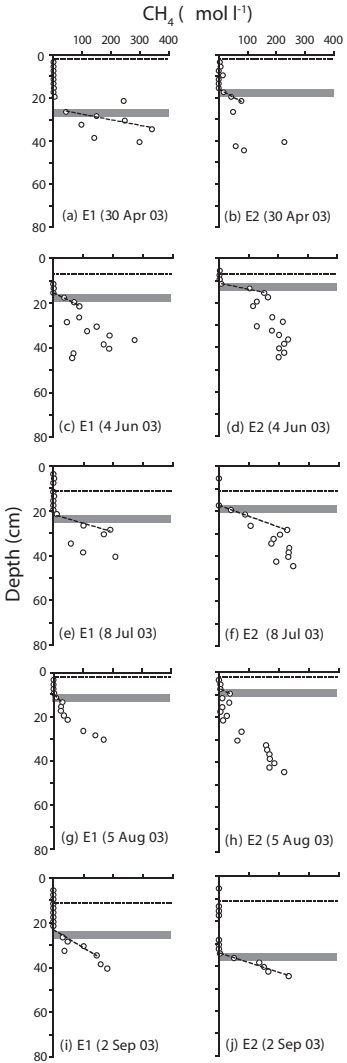

Fig. 5. Pore water profiles of dissolved CH_4 measured at Blaen Fign during the summer of 2003 from pore water equilibrators E1 and E2. Water-table level in each panel is indicated by a dotted horizontal line. The dashed line through shallow CH_4 values trending to zero concentration is a regression line fitted to the data to determine the gradient $d[CH_4]/dz$, which was used to calculate rates of CH_4 flux into the methanotrophic zone.

BGD
5, 2607–2643, 2008

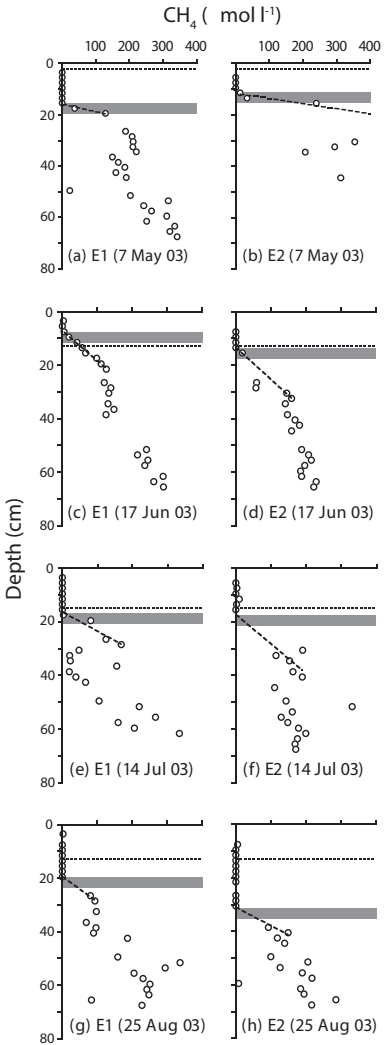

Fig. 6. Pore water profiles of dissolved CH_4 measured at Cors Caron during the summer of 2003 from pore water equilibrators E1 and E2. Water-table level in each panel is indicated by a dotted horizontal line. The dashed line through shallow CH_4 values trending to zero concentration is a regression line fitted to the data to determine the gradient $d[CH_4]/dz$, which was used to calculate rates of CH_4 flux into the methanotrophic zone.

BGD
5, 2607–2643, 2008

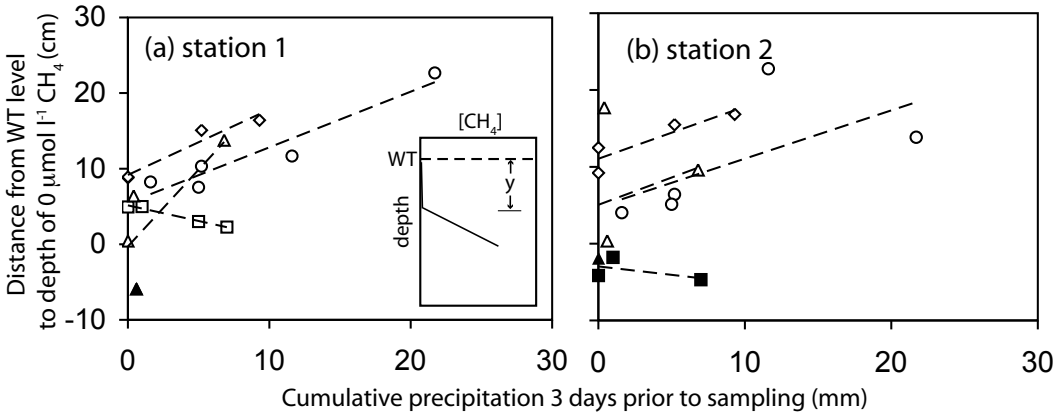

Fig. 7. Distance from water table surface to depth of nil CH_4 concentration plotted against the cumulative amount of precipitation from the 3-day period prior to collection of the pore water CH_4 samples. The y-axis parameter is explained graphically in the inset to panel **(a)**. Y-axis data in panels (a) and **(b)** are from stations 1 and 2, respectively, at each peatland. The symbols correspond to Crymlyn Bog (squares), Cors Caron (triangles), Blaen Fign (circles), and Gors Lywd (diamonds). Filled symbols represent times when $[CH_4]$ was $>0\,\mu mol\,l^{-1}$ at the air-water interface. Precipitation data (shown in Fig. 2) were taken from Swansea Victoria Park (src id 1257) for Crymlyn Bog, Swyddffynnon (src id 1204) for Cors Caron, and Cwmystwyth (src id 1211) for Blaen Fign and Gors Lywd. The dashed lines are linear regression analysis curves fitted to the data for each peatland. The equations for the eight regression lines are listed in Table 4.

BGD
5, 2607–2643, 2008